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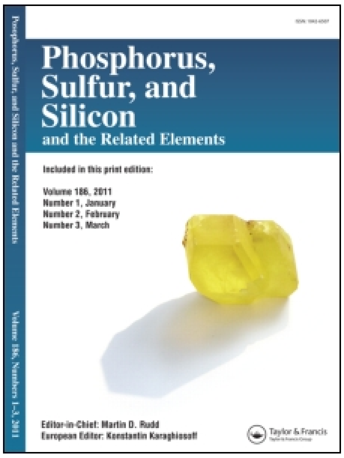

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Risto S. Laitinen; Arto Maaninen; Jarkko Pietikäinen

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SELENIUM- AND TELLURIUM-CONTAINING CHALCOGEN NITRIDES

RISTO S. LAITINEN, ARTO MAANINEN and
JARKKO PIETIKÄINEN
Department of Chemistry, University of Oulu, Linnanmaa, 90570 Oulu,
Finland

The recent progress in the chemistry of electrically neutral selenium- and tellurium-containing chalcogen nitrides is reviewed. The synthetic and structural aspects of the eight-membered E_4N_4, six-membered E_4N_2, and E_2N_2 are described.

Keywords: Chalcogen nitrides, X-ray diffraction, NMR spectroscopy, *Ab initio* calculations

INTRODUCTION

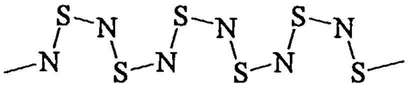
The chemistry of sulfur-nitrogen compounds is one of the main areas in current inorganic research (see Refs.1 and 2 for recent reviews). While the field is relatively old dating back to the first preparation of S_4N_4 in 1830's (for the early history of sulfur-nitrogen compounds, see Ref. 3), it is only in the recent decades that the advent of modern structural methods has brought considerable progress in the structural characterization of a wide variety of molecular species.

The chemistry of selenium-nitrogen and tellurium-nitrogen compounds has seen much slower progress than that of sulfur-nitrogen species.[4,5] This is largely due to the instability of the selenium- and tellurium-containing species. The structure of Se_4N_4, however, is known [6-10] and the existence of Te_3N_4 has been suggested.[11] In addition both selenium and tellurium imides have been prepared and structurally characterized.[12-14]

The main challenge in the extensive research carried out for heterocyclic sulfur-nitrogen compounds was originally to understand the unexpected structural and bonding properties of these species. It was recently discovered, however, that polymeric sulfur nitride $(SN)_x$ has anisotropic semiconducting properties and that it becomes superconducting below 0.33 K.[15] This discovery has boosted the activity in the synthetic and structural work of sulfur-nitrogen compounds.

$(SN)_x$ is best prepared by the solid state polymerization of cyclic S_2N_2 at room temperature, though other routes to produce this material are also known. For instance, the reaction of $S_3N_2Cl_2$ or $(NSCl)_3$ with Me_3SiN_3 also produces the polymer.[16] It has also been observed that other heterocyclic sulfur-nitrogen species can serve as precursors for $(SN)_x$.

$(SN)_x$ has a bluish colour with a bronze reflection and metallic lustre. Its crystal structure has shown an almost planar polymer:



The two S-N bonds have bond orders of about 1.5, but are not exactly equal.[17] $(SN)_x$ conducts electricity in the direction of the S-N chains, but is a much poorer conductor perpendicular to the chains. The partial bromination of the polymer yields $(SNBr_{0.4})_x$ the conductivity of which is of an order of magnitude greater than that of the parent polymer.[15]

$(SeN)_x$, $(TeN)_x$, and the mixed chalcogen-nitrogen polymers could also be expected to have interesting electrical properties. Up to present, however, their preparation and characterization have not been reported, probably because of the instability of the heterocyclic precursors.

In this work we report the recent progress in the preparation and characterization of mixed chalcogen-nitrogen heterocycles. The goal is to find usable precursors for the polymeric chalcogen nitrides and to establish the plausibility of the polymer production.

$Se_xS_{4-x}N_4$

The molecular structure of tetrasulfur tetranitride exhibits a cage with two short transannular S···S bonds (see Figure 1).[18] Se_4N_4 has two different polymorphs. One is isostructural with S_4N_4.[10] The second polymorph shows a similar molecular structure but different packing of the molecules. Our recent *ab initio* molecular orbital calculations at HF/MIDI-4* level of theory for all members of the $Se_xS_{4-x}N_4$ series shows that the analogous molecular geometry in all possible species is the true global energy minimum.[19]

It is well known that both S_4N_4 and Se_4N_4 are very unstable and explode easily upon heating. Se_4N_4 in particular is very explosive. Our

TABLE I. **Total MP2/MIDI-4*//MIDI-4* binding energies in $Se_xS_{4-x}N_4$ (in kJ mol^{-1})** [19]

Molecule	MP2/MIDI-4*	Exptl.
S_4N_4	1758	2408 [a]
SeS_3N_4	1684	
$Se_2S_2N_4$	1621	
	1626	
Se_3SN_4	1552	
Se_4N_4	1494	1976 [b]

[a] Ref. [20]. [b] Ref. [21]

calculations on the relative energies of $Se_xS_{4-x}N_4$ at MP2/MIDI-4*//MIDI-4* level of theory indicates a steadily decreasing stability as a function of the selenium content in the molecule (see Table I). The relative stabilities indicate, however, that it should be possible to prepare mixed eight-membered sulfur-selenium nitrides.

There are several traditional methods to produce both S_4N_4 [1,2] and Se_4N_4.[4] We have recently reported convenient preparations for both compounds utilizing bis(trimethylsilyl)amino chalcogenides and chalcogen chlorides:[22,23]

$$[(Me_3Si)_2N]_2S + SCl_2 + SO_2Cl_2 \rightarrow \tfrac{1}{2}\, S_4N_4 + 4\, Me_3SiCl + SO_2$$

$$[(Me_3Si)_2N]_2Se + SeCl_4 \rightarrow \tfrac{1}{2}\, Se_4N_4 + 4\, Me_3SiCl$$

These reactions can conveniently be applied for the production of an eight-membered selenium sulfur nitride:

$[(Me_3Si)_2N]_2Se + SCl_2 + SO_2Cl_2 \rightarrow ½\ Se_2S_2N_4 + 4\ Me_3SiCl + SO_2$

$[(Me_3Si)_2N]_2S + SeCl_4 \rightarrow ½\ Se_2S_2N_4 + 4\ Me_3SiCl$

Both reactions produce $Se_2S_2N_4$ in good yields (*ca.* 70 %). The compound was identified as 1,5-$Se_2S_2N_4$ by X-ray crystallography, ^{14}N and ^{77}Se NMR spectroscopy, mass spectroscopy, and vibrational spectroscopy.

The molecular structure of $Se_2S_2N_4$ is shown in Fig. 1. The molecule is isostructural with S_4N_4 [18] and β-Se_4N_4 [10] and exhibits a similar cage-structure. All chalcogen-atom positions are, however, disordered containing 50 % of both selenium and sulfur. This is also reflected in the bond lengths that all show intermediate values between those of S_4N_4 and Se_4N_4. It is not possible, however, from the crystal structure alone to deduce whether the crystalline phase is a solid solution of S_4N_4 and Se_4N_4 or a real ternary compound $Se_2S_2N_4$.

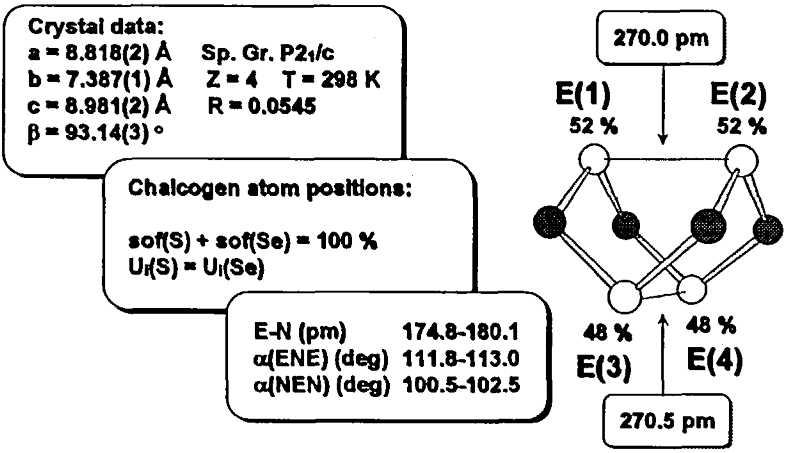
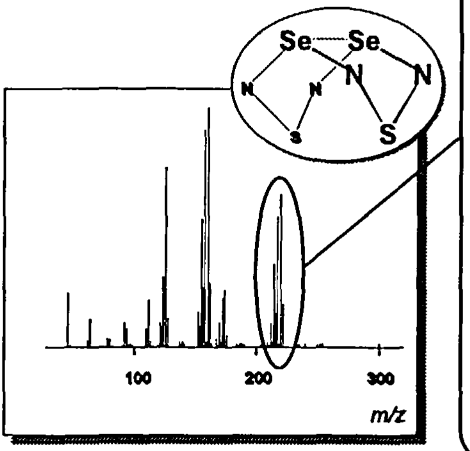


FIGURE 1. The crystal and molecular structure of $Se_2S_2N_4$. Open circles denote chalcogen atoms and the shaded ones nitrogen atoms. The percentages in the figure denote the site occupation factors (sof) of selenium.

The ^{14}N NMR spectrum of the compound exhibited a single resonance at –238 ppm. The value is reasonable for $Se_2S_2N_4$ when compared to –257 ppm observed for S_4N_4.[24] The ^{77}Se NMR spectrum also exhibited a single resonance at 1418 ppm. Both these signals are consistent with the 1,5-isomer of $Se_2S_2N_4$. In the case of the 1,3-isomer three resonances at the intensity ratio of 2:1:1 would be expected in the ^{14}N NMR spectrum. Furthermore, the two methods of preparation also imply the formation of the 1,5-isomer.

The 12 eV EI mass spectrum of the product is shown in Fig. 2. It can be seen from the figure that the fragment of highest mass is $Se_2SN_2^+$. The appearance of this fragment also indicates the parent molecule as 1,5-$Se_2S_2N_4$.



Se_2SN_2

m/z	I_{calc}	I_{obs}
210	0.5	-
211	0.4	-
212	4.1	3.6
213	4.6	4.1
214	19.1	18.3
215	12.3	11.9
216	49.5	48.4
217	26.2	25.3
218	85.4	83.2
219	7.0	6.9
220	100.0	100.0
221	1.7	1.6
222	34.5	33.9
223	0.5	-
224	4.1	3.2

FIGURE 2. The 12 eV EI mass spectrum of $Se_2S_2N_4$

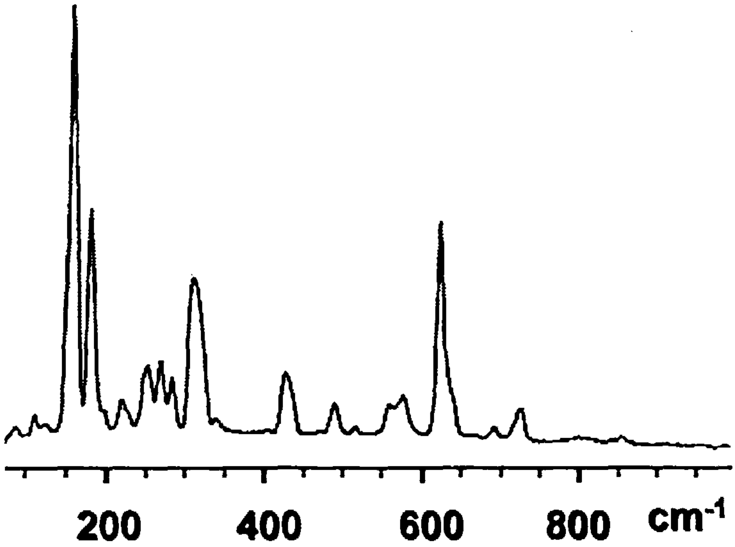


FIGURE 3. The Raman spectrum of $Se_2S_2N_4$ recorded at –100 °C.

The Raman spectrum of $Se_2S_2N_4$ is shown in Fig. 3. The fundamental vibrations were calculated for 1,5-$Se_2S_2N_4$ by use of a General valence force field and resulted in a good agreement between the calculated values and the observed Raman lines. The calculations also yielded reasonable values of the force constants when compared to those of some related species (see Table II).

TABLE II. The stretching force constants in 1,5-$Se_2S_2N_4$ and related compounds (in N m^{-1}).

Molecule	$f_{S\text{-}N}$	$f_{Se\text{-}N}$	$f_{S\text{-}S}$	$f_{Se\text{-}Se}$
$Se_2S_2N_4$	355	252	36	78
S_4N_4	353		55	
Se_4N_4		239		76
S_4N_4 [a]	376		21	
$S_4(NH)_4$ [b]	401			

[a] Ref. [25]. [b] Ref. [26]

The Attempted Preparation of $Te_2S_2N_4$

An attempt was made to produce 1,5-$Te_2S_2N_4$ by utilizing a similar approach as was used in the successful preparation of the analogous selenium sulfur nitride described above:

$$[(Me_3Si)_2N]_2Te + SCl_2 + SO_2Cl_2 \rightarrow \tfrac{1}{2}\ 1,5\text{-}Te_2S_2N_4 + 4\ Me_3SiCl + SO_2$$

Pale yellow needle-like, air-sensitive crystals were formed. The crystal structure determination (see Fig. 4) indicated that instead of the desired product, the chlorination of the tellurium atom in bis[bis(trimethylsilyl)amino]telluride had taken place. The reaction could be carried out in a good yield by involving SO_2Cl_2 only:

$[(Me_3Si)_2N]_2Te + SO_2Cl_2 \rightarrow [(Me_3Si)_2N]_2TeCl_2 + SO_2$

The compound exhibited a ^{14}N NMR resonance at -312 ppm and a ^{125}Te NMR signal at 1515 ppm. As seen in Fig. 4. the crystal structure showed a four-coordinate tellurium of trigonal bipyramidal geometry. The two chlorine atoms occupied the axial positions, and the lone-pair and the two bis(trimethylsilyl)amino groups the three equatorial positions. Both Te-N bonds show single bond lengths.[14] It is interesting to note that the two approximately coplanar Te-N(-Si)$_2$ fragments lie in different orientations. One fragment lies on the axial plane and the other on the equatorial plane.

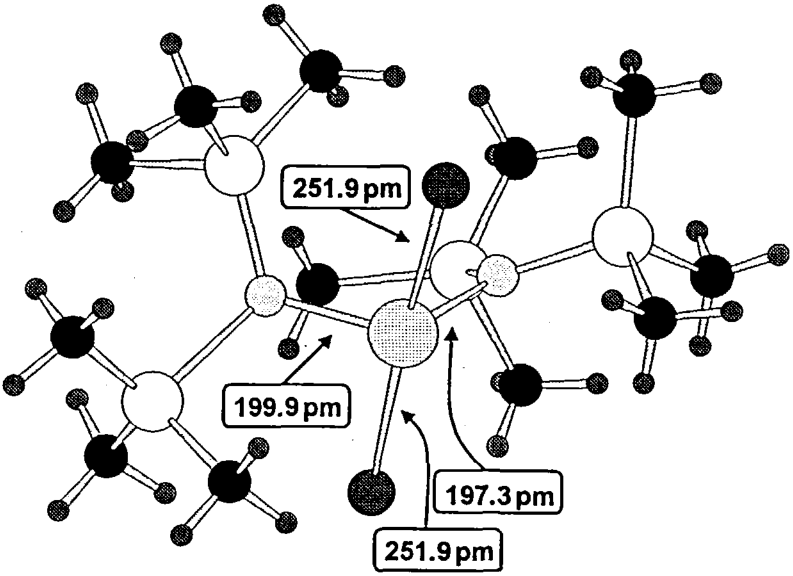


FIGURE 4. The molecular structure of $[(Me_3Si)_2N]_2TeCl_2$. Crystal data: $a = 8.517$, $b = 11.667$, $c = 24.376$ Å, $\beta = 91.05$ °, $R = 0.0493$.

E_4N_2

While S_4N_2 is well-known, the existence of Se_4N_2 is under debate. Dehnicke *et al.* [27] has reported its preparation from dichlorodiselane and trimethylsilyl azide in dichloromethane, but a closer examination has revealed that this reaction produces $Se_3N_2Cl_2$.[28] Our recent *ab initio* calculations [29] have indicated two trends in the stability of the different memebers in the $Se_xS_{4-x}N_2$ series: The stability decreases with increasing selenium content, and for the given chemical composition the isomers containing the N=Se=N unit are less stable than those containing the N=S=N unit. The latter energy relationship may explain the lack of formation of Se_4N_2.

The reaction of $[(Me_3Si)_2N]_2S$ with a 3:1:1 mixture of S_2Cl_2, Se_2Cl_2, and $SeCl_4$ produced a heterocyclic six-membered species that was inferred to be $\overline{\mathrm{SSeSNSN}}$ on the basis of the elemental analysis, mass spectroscopy, vibrational analysis, and NMR spectroscopy.[29]

E_2N_2

It is well-known that a gas-phase decomposition of S_4N_4 over silver wool yields S_2N_2 that will eventually polymerize to $(SN)_x$.[15] The MIDI-4* calculations show that the structures of all four-atomic E_2N_2 (E = S, Se, Te) ring molecules are very similar (see Fig. 5). It can be seen that there is an interesting structural trend: As the electronegativity of the chalcogen atom decreases, the bond lengths involving the second chalcogen atom diagonally across the ring become shorter.

The total binding energies that have been calculated at MP2/MIDI-4*//MIDI-4* level of theory expectedly decrease as the selenium and tellurium content in the ring increases (see Fig. 6). The trends imply, however, that all species should be stable enough to enable their preparation.

It is interesting to note that the energy change in the decomposition of the $Se_xS_{4-x}N_4$ to cyclic four-atomic species increases dramatically as the selenium content of the molecules increases (see Table III). This may well provide a barrier for the formation of E_2N_2 species containing selenium and tellurium and thus have an effect on the formation of selenium- and tellurium-containing polymers, especially as the volatility of the eight-membered species decreases with increasing selenium content and thus renders the gas phase reaction unlikely.

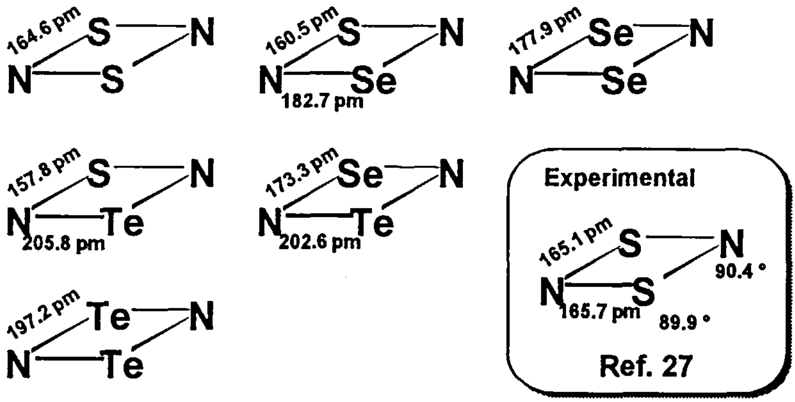


FIGURE 5. The HF/MIDI-4* optimized geometries of E_2N_2 (E = S, Se, Te).

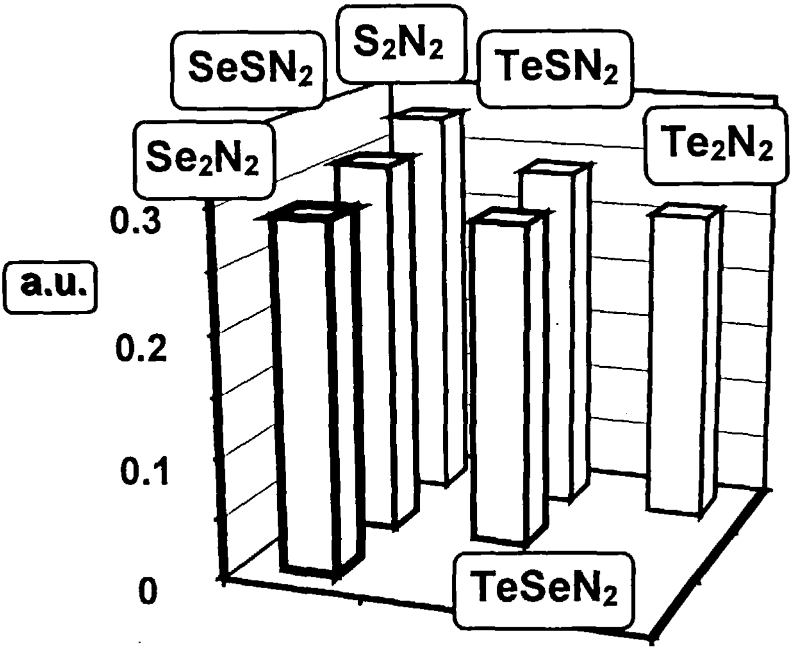


FIGURE 6. The total MP2/MIDI-4*//MIDI-4* binding energies of E_2N_2 (E = S, Se, Te)

TABLE III. The MP2/MIDI-4*//MIDI-4* decomposition energies of $Se_xS_{4-x}N_4$.

Reaction			ΔH (kJ mol^{-1})
S_4N_4	→	2 S_2N_2	9.9
SeS_3N_4	→	$SeSN_2$ + S_2N_2	23.8
1,3-$Se_2S_2N_4$	→	Se_2N_2 + S_2N_2	40.3
1,3-$Se_2S_2N_4$	→	2 $SeSN_2$	44.4
1,5-$Se_2S_2N_4$	→	2 $SeSN_2$	49.1
Se_3SN_4	→	Se_2N_2 + $SeSN_2$	58.6
Se_4N_4	→	2 Se_2N_2	79.3

(EN)$_x$

The polymerization of S_2N_2 to form polymeric sulfur nitride $(SN)_x$ is accompanied by an increase and eventual decrease of an esr signal that mplies that the reaction proceeds with a radical mechanism.[15] It has been pointed out that S_2N_2 has low-lying singlet and triplet diradical states.[31] Our *ab initio* comparison [32] of E_2N_2 species containing sulfur, selenium, and tellurium at varying proportions have indicated that as long as the four-membered molecule contains sulfur, the energy of the triplet state lies near to the singlet ground state, but with species containing selenium and tellurium, the analogous triplet state lies significantly higher in energy rendering this path of polymerization unlikely.

We have performed preliminary attempts to polymerize 1,5-$Se_2S_2N_4$ by subliming the material through a silver gauge. A blue-violet material was obtained that showed a ^{14}N NMR signal at –128 ppm and a highest fragment in the mass spectrum at *m/z* 139 (see Fig. 7). The fragmentation pattern is consistent with the presence of $SeSN_2$. Further characterization of the blue-violet product is currently in progress.

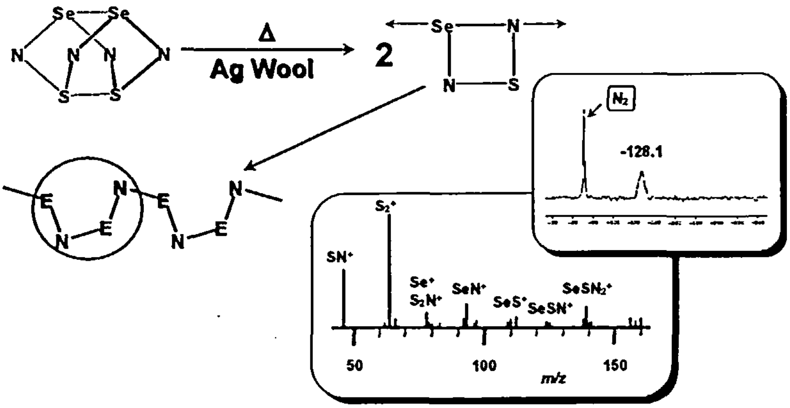


FIGURE 7. The ^{14}N NMR and mass spectrum of a product obtained upon sublimation of 1,5-$Se_2S_2N_4$ over the silver wool.

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